Abs. 574, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Solid-State Redox Reaction of $LiNi_{1/2}Mn_{1/2}O_2$ for Advanced Lithium-Ion Batteries

Tsutomu Ohzuku and Yoshinari Makimura

Graduate School of Engineering, Osaka City University (OCU), Osaka 558-8585, Japan

In recent years, there has been increasing interest in lithium nickel manganese oxides with or without cobalt for advanced lithium-ion batteries [1-5]. In a previous paper [5], we have shown that $LiNi_{1/2}Mn_{1/2}O_2$ is a stable compound consisting of Ni^{2+} and Mn^{4+}, not a solid solution of $LiNiO_2$ and $LiMnO_2$, whereas $LiCo_{1/2}Ni_{1/2}O_2$ is a one-to-one solid solution of $LiCoO_2$ and $LiNiO_2$. Our main concern is electrochemistry of lithium insertion materials rather than crystal and electronic structures, which complement our understanding on lithium insertion materials. In this paper, we examine the solid-state redox reaction of $LiNi_{1/2}Mn_{1/2}O_2$ by applying a concept of electrochemical density of states [6], and the results are compared with those of $LiNiO_2$ and $LiCo_{1/2}Ni_{1/2}O_2$.

Figure 1 (b) shows the results on reversible potential measurements of $Li_yNi_{1/2}Mn_{1/2}O_2$. As shown in Fig. 1, the solid-state redox reaction of $LiNi_{1/2}Mn_{1/2}O_2$ can be illustrated by decomposing the system into three parts at y = 1/3 and 2/3 in $Li_yNi_{1/2}Mn_{1/2}O_2$, which are characterized by 4.49, 4.05, and, 3.81 V of redox levels. Negative interaction parameters of $z\phi_i/F$ mean repulsive interaction, i.e., one-phase reaction over an entire range.

Although nickel manganese dioxide ($\square Ni_{1/2}Mn_{1/2}O_2$) cannot be obtained due to the thermodynamic limitation, we can calculate the Gibbs free energy change for the overall reaction. The Gibbs free energy change is calculated to be –396 $kJ \cdot mol^{-1}$ by integrating $E(y)$ in the composition range of $0 \leq y \leq 1$, corresponding to the average voltage of 4.10 V. The average voltage of 4.10 V for $LiNi_{1/2}Mn_{1/2}O_2$ is higher than 3.90 V for $LiNiO_2$, which is almost the same as 4.08 V for $LiCo_{1/2}Ni_{1/2}O_2$ [6].

Figure 2 shows the levels of solid-state redox potentials for $LiNi_{1/2}Mn_{1/2}O_2$, $LiNiO_2$, and $LiCo_{1/2}Ni_{1/2}O_2$. The solid-state redox reaction for $LiNiO_2$ formally consists of Ni^{3+}/Ni^{4+} and that for $LiNi_{1/2}Mn_{1/2}O_2$ seemingly consists of Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+}. Difference in average voltage associated with redox reaction of nickel species for both samples is 0.3 V. When we compare average voltage of $LiCo_{1/2}Ni_{1/2}O_2$ with that of $LiNi_{1/2}Mn_{1/2}O_2$, both samples shows the same voltage in spite of different redox species.

From these results, we will discuss characteristic features on solid-state redox reactions of lithium insertion materials for advanced lithium-ion batteries.

References

1. T. Ohzuku and Y. Makimura, *Chem. Lett.*, **30**, 744 (2001).
2. Z. Lu, D. D. MacNeil, and J. R. Dahn, *Electrochem. Solid-State Lett.*, **4**, A191 (2001).
3. Y. Makimura and T. Ohzuku, *J. Power Sources*, **119-121**, 156 (2003).
4. B. J. Hwang, Y. W. Tsai, D. Carlier, and G. Ceder, *Chem. Mater.*, **15**, 3676 (2003).
5. Y. Koyama, Y. Makimura, I. Tanaka, H. Adachi, and T. Ohzuku, *J. Electrochem. Soc.*, in press (2004).
6. T. Ohzuku and A. Ueda, *J. Electrochem. Soc.*, **144**, 2780 (1997).

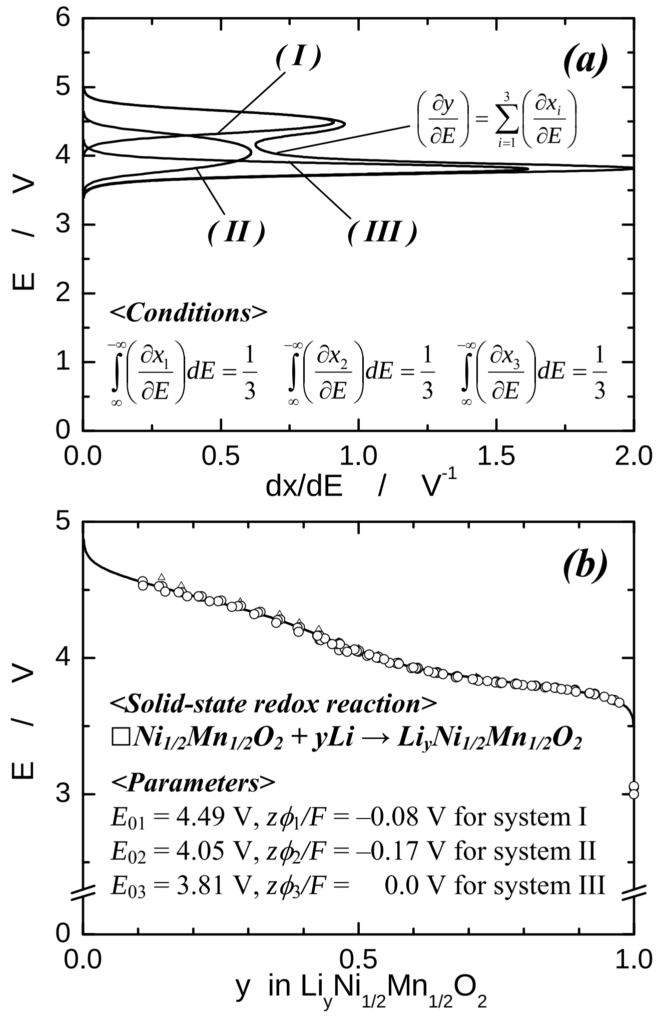

Fig. 1 (a) The E versus (dx/dE) curves together with the E versus (dy/dE) curve for the solid-state redox reaction of $LiNi_{1/2}Mn_{1/2}O_2$. (b) Comparison between the observed reversible potentials (open circles) and calculated $E(y)$ (solid line) curves. The E versus y curve is obtained by integrating (dy/dE) with respect to E from plus infinity to E.

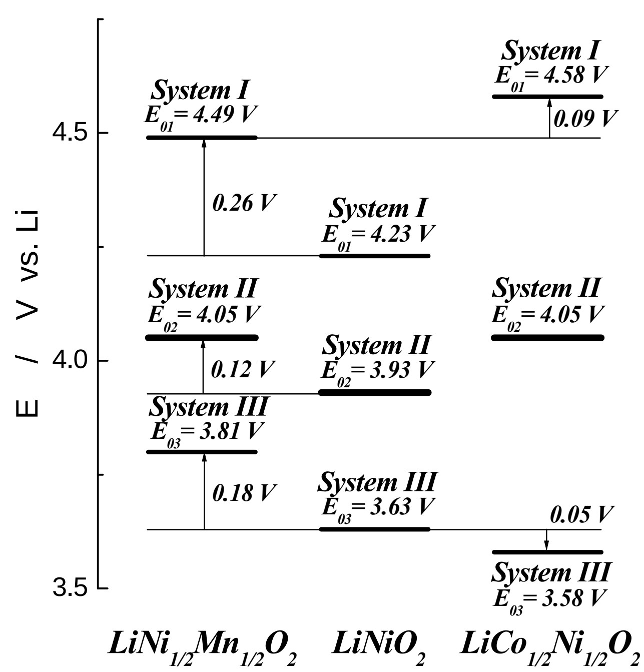

Fig. 2 Levels of the solid-state redox potentials for $LiNi_{1/2}Mn_{1/2}O_2$, $LiNiO_2$, and $LiCo_{1/2}Ni_{1/2}O_2$.